CURABLE COMPOSITION

BACKGROUND OF THE INVENTION

(1) Field of the Invention

This invention relates to a curable composition comprising a specific aromatic dibasic acid having an ethylenically unsaturated group, such as 4-methacryloxyethyltrimellitate or its anhydride, an ethylenically unsaturated monomer other than said aromatic dibasic acid and a catalyst. More particularly, the invention relates to a curable composition valuable as a dental adhesive or cement or as an undercoating agent for an adhesive or paint.

(2) Description of the Prior Art

Curable compositions comprising an acrylic or methacrylic monomer such as methyl methacrylate, 2,2-bis(p-2'-hydroxy-3'-methacryloxypropoxyphenyl)propane or the like and a free-radical initiator have been proposed and used as dental adhesives or cements.

These conventional compositions, however, are still insufficient in the bonding force to enamel of teeth. Accordingly, when teeth are treated with these compositions, it is necessary to treat enamel of the teeth in advance with a strong acid and then conduct the bonding operation. Therefore, the tooth treatment becomes troublesome and enamel on the surface of a tooth is worn away by the acid treatment. It has been desired to eliminate these disadvantages involved in the conventional compositions.

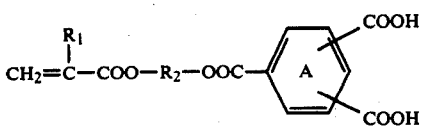
BRIEF SUMMARY OF THE INVENTION

We found that when a curable composition comprising a specific aromatic dibasic acid having an ethylenically unsaturated group such as 4-methacryloxyethyltrimellitate, an ethylenically unsaturated monomer other than said aromatic dibasic acid and a catalyst is used as a dental adhesive, the composition has a strong adhesiveness to either enamel or dentin of a tooth and the resulting bonded structure is prominently excellent in such properties as water resistance and durability.

It is therefore a primary object of this invention to provide a curable composition which has an excellent adhesiveness to the tooth tissue or a substrate such as a metal and can give a bonded structure excellent in the water resistance and durability.

Another object of the present invention is to provide a curable composition which can be applied to the tooth tissue or a substrate metal without use of a solvent and can be polymerized and cured in situ to form an adhesive layer or undercoat layer.

In accordance with the present invention, there is provided a curable composition comprising (A) an ethylenically unsaturated carboxylic acid represented by the following general formula:



(1)

wherein

R_1 is a hydrogen atom or a methyl group,

R_2 is an alkylene group having 2 to 4 carbon atoms, and in the benzene ring A two carboxyl groups are bonded to carbon atoms other than the carbon atoms adjacent to the carbon atoms to which the ester group is bonded,

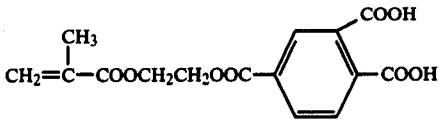
or an acid anhydride thereof, (B) at least one ethylenically unsaturated monomer other than said monomer (A), said ethylenically unsaturated monomer (B) being copolymerizable with said monomer (A), and (C) at least one catalyst selected from the group consisting of free radical initiators and photosensitizers.

DETAILED DESCRIPTION OF THE INVENTION

In the ethylenically unsaturated carboxylic acid or its anhydride (A) that is used in the present invention, it is important that two carboxyl groups or one acid anhydride group should be present on the benzene ring, and that in the benzene ring, two carboxyl groups or one acid anhydride group should be bonded to carbon atoms other than the carbon atoms adjacent to the carbon atom to which the ester group is bonded.

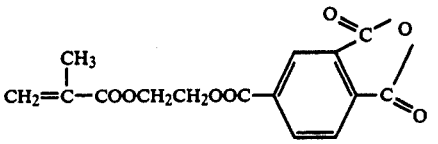
A curable composition comprising an ethylenically unsaturated carboxylic acid or its anhydride having the above-mentioned chemical structure has a prominently excellent adhesiveness over a curable composition comprising an ethylenically unsaturated carboxylic acid having one carboxyl group on the benzene ring or an ethylenically unsaturated carboxylic acid having in the benzene ring a carboxyl group bonded to the carbon atom adjacent to the carbon atom to which the ester group is bonded.

An ethylenically unsaturated carboxylic acid or its anhydride most preferred for attaining the objects of the present invention is 4-methacryloxyethyltrimellitate (melting point=119.5° to 120.0° C.) having the following formula:



(2)

or its anhydride (melting point=95.0° to 95.8° C.) having the following formula:



(3)

The monomer of the formula (3) may be prepared by dehydrochlorination reaction between hydroxyethyl methacrylate and anhydrous trimellitic acid chloride or by dehydration reaction between hydroxyethyl methacrylate and trimellitic anhydride. 4-Methacryloxyethyltrimmellitate of the formula (2) can easily be prepared by hydration of 4-methacryloxyethyltrimellitate anhydride.

These acid and acid anhydride may be used singly or in the form of a mixture thereof.

As examples of other ethylenically unsaturated carboxylic acids and acid anhydrides that can be used in the present invention, there can be mentioned 4-methacryloxy-3'-propyltrimellitate and its anhydride, 4-acryloxyethyltrimellitate and its anhydride, 4-methacryloxy-4'-butyltrimellitate and its anhydride, and 5-methacryloxyethyltrimesic acid.